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Special

BOUNDARY LAYER BUILDUP IN THE DEMINERALIZATION OF SALT WATER BY REVERSE OSMOSIS

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BOUNDARY LAYER BUILDUP IN THE DEMINERALIZATION OF SALT WATER BY REVERSE OSMOSIS**

by

Lawrence Dresner

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*Work performed for the Office of Saline Water, U. S. Department of the Interior, at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission.

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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UNION CARBIDE CORPORATION
for the
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BOUNDARY LAYER BUILDUP IN THE DEMINERALIZATION OF SALT WATER BY REVERSE OSMOSIS[1]

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ABSTRACT

The buildup of saline boundary layers adjacent to permselective membranes has been studied. Two situations have been considered. In the first, water is forced by a piston through a semipermeable membrane; there is no lateral flow of the water over the face of the membrane. The salt concentration at the surface of the membrane increases monotonically with time and is asymptotically linear in the time. In the second situation, the pressurized feed solution flows continuously through a channel whose walls are made of the semipermeable membrane. The flow may be either laminar or turbulent. In the laminar case, formulas for the salt concentration at the wall in both the asymptotic region ("well-developed" concentration profile) and the entrance region (boundary-layer region) have been derived. In the turbulent case, a simple formula for the salt concentration at the wall has been derived from the Chilton-Colburn analogy.

(1) Work performed for the Office of Saline Water, U. S. Department of the Interior, at the Oak Ridge National Laboratory, Oak Ridge, Tennessee operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission.

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Introduction

Salt water can be purified by pumping it under pressure through a membrane more permeable to water than to salt.[2] Most promising among the

(2) C. E. Reid and E. J. Breton, J. App. Polymer Sci. 1 133 (1959).

materials from which semipermeable membranes can be prepared is cellulose acetate,[3] but other organic polymers can also serve.[4] When water is being

(3) C. E. Reid and E. J. Breton, op. cit.; "Sea Water Demineralization by Means of a Semipermeable Membrane," S. Loeb and S. Sourirajan, UCLA Report No. 60-60, July, 1960.
(4) C. E. Reid and E. J. Breton, op. cit.; S. Loeb and S. Sourirajan, "Sea Water Demineralization by Means of an Osmotic Membrane," Advances in Chemistry Series #38, Amer. Chem. Soc., 1963, p. 117.

pumped through such a membrane, the salt it keeps back concentrates in a highly saline boundary layer immediately adjacent to the membrane surface. Buildup of such a boundary layer has several serious consequences: it raises the local osmotic pressure of the water and so decreases the driving force available for reverse osmosis, it increases the salt content of the water coming through the membrane, and it may cause the precipitation of relatively insoluble scale-forming salts.

The buildup of a salt-rich layer along side the membrane has been termed the "concentration polarization" of the membrane by K. A. Kraus. This paper is devoted to estimating the extent of concentration polarization in two simple prototype desalting cells.

The simplest imaginable batch-operated cell is just a cylinder closed by the semipermeable membrane at one end and a piston at the other. The simplest imaginable continuously operated cell is a channel of some sort whose walls are made of the semipermeable membrane (backed by a suitable supporting material) and which contains the pressurized feed solution. In this second cell, fresh feed solution flows continuously through the channel; this flow may be either laminar or turbulent.

Owing to its penetration of the channel walls, the water has an average "radial" component of velocity that is ordinarily absent in laminar channel flow. Furthermore, the velocity profile of the axial flow is affected by the "radial" motion of the water. Berman[5] has

(5) A. S. Berman, Proceedings of the Second International Conference at Geneva on the Peaceful Uses of Atomic Energy **4** 351 (1958). This paper contains references to earlier work.

solved the problem of fully developed laminar channel flow with both fluid injection and removal at the channel wall for rectangular, cylindrical, and annular channels. Using his radial and axial fluid velocity profiles, we shall calculate the radial and axial concentration profiles of the salt in the channel.

When the channel flow is turbulent, nothing is known of the effect of fluid removal at the wall on the fluid velocity distribution, and we shall perforce neglect this effect in calculating the concentration profile of the salt.

Batch-Operated Cell

If the radius and length of the cylindrical batch-operated cell are large enough, the problem of calculating the axial concentration profile becomes the problem of an infinite mass of fluid moving uniformly against a plane, semipermeable interface. The geometry is shown in Fig. 1.

The differential equation governing diffusion in a moving fluid is

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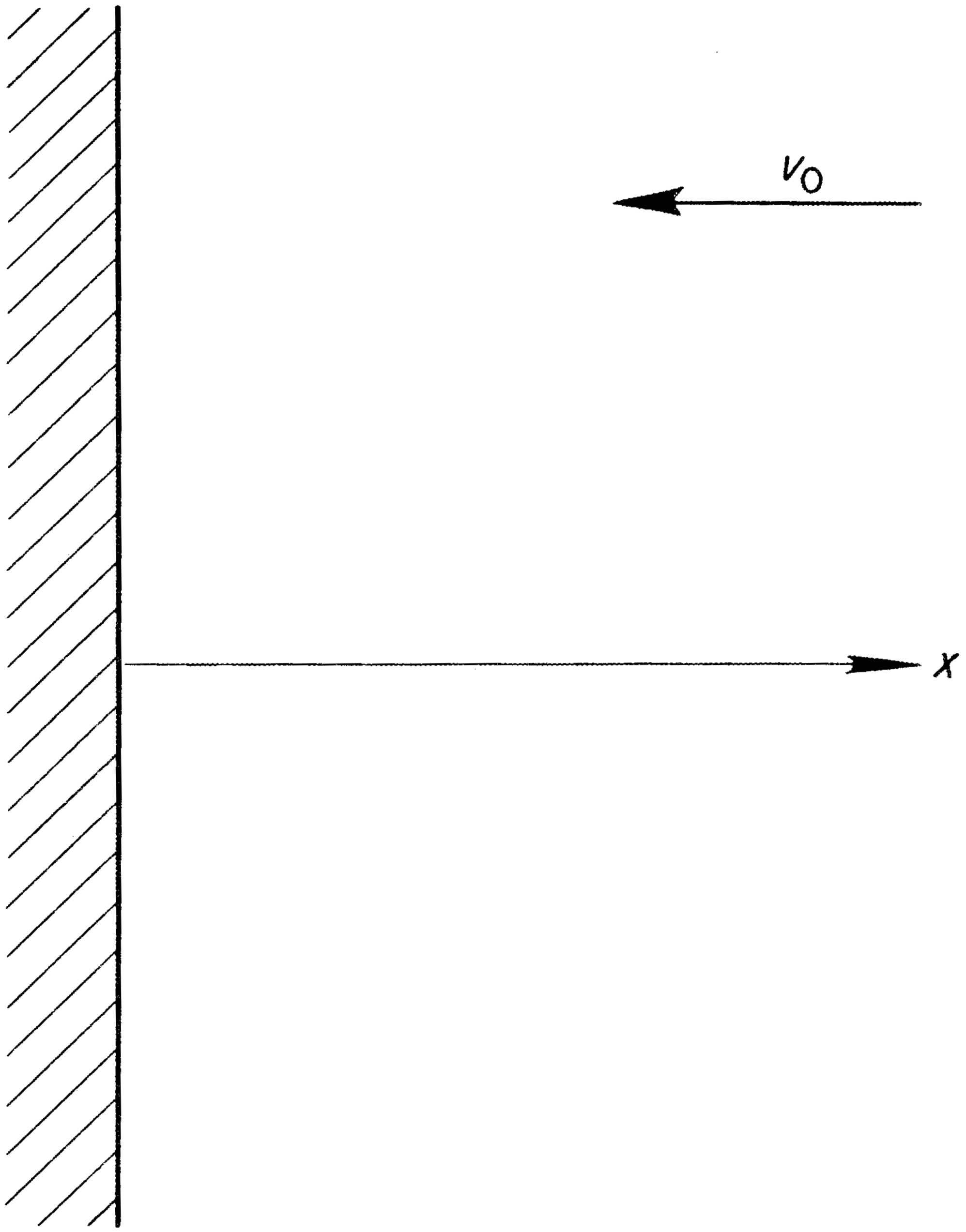

Fig. 1. The Idealized Geometry of the Batch-Operated Cell.

$$\frac{\partial c}{\partial t} + v \cdot \text{grad } c = \mathcal{D} \nabla^2 c \tag{1}$$

In the geometry of Fig. 1, this simplifies to

$$\frac{\partial c}{\partial t} - v_o \frac{\partial c}{\partial x} = \mathcal{D} \frac{\partial^2 c}{\partial x^2} \tag{2}$$

We must solve Eq. (2) subject to the boundary conditions

$$c(x, o) = c_o \tag{3a}$$

$$v_o\, c(o,t) + \mathcal{D} \left(\frac{\partial c}{\partial x} \right)_{\substack{x=o \\ t=t}} = 0 \tag{3b}$$

Eq. (3b) says that the net current of salt across the membrane at $x = 0$ is zero.

For simplicity, let us introduce the following dimensionless variables:

$$\Gamma = \frac{c - c_o}{c_o} \tag{4a}$$

$$\xi = \frac{v_o x}{\mathcal{D}} \tag{4b}$$

$$\tau = \frac{v_o^2\, t}{\mathcal{D}} \tag{4c}$$

In terms of these variables (2) and (3) become

$$\frac{\partial^2 \Gamma}{\partial \xi^2} + \frac{\partial \Gamma}{\partial \xi} = \frac{\partial \Gamma}{\partial \tau} \tag{5a}$$

$$\left(\frac{\partial \Gamma}{\partial \xi} \right)_{\substack{\xi=0 \\ \tau=\tau}} + \Gamma(0, \tau) = -1 \tag{5b}$$

$$\Gamma(\xi, 0) = 0 \tag{5c}$$

Henceforth, the variable Γ will be called the concentration polarization.

Interestingly, the system of equations (5) has no steady-state solution: the salt concentration at the membrane rises monotonically with time. Asymptotically, i.e., for large τ, Γ varies linearly with τ. To show this, let us begin by integrating (5a) over all ξ. Using (5b), we find the result

$$\frac{\partial}{\partial\tau}\int_0^\infty \Gamma(\xi,\tau)\ d\xi = 1 \tag{6a}$$

or its equivalent

$$\int_0^\infty \Gamma(\xi,\tau)\ d\xi = \tau \tag{6b}$$

No constant of integration appears in (6b) because Γ vanishes when $\tau = 0$ (Eq. 5c).

For large τ, we might expect the salt concentration profile to assume a constant shape and only change in magnitude. This consideration suggests we try a solution of the type $\tau\Xi_1(\xi) + \Xi_2(\xi)$, where Ξ_1 and Ξ_2 are as yet undetermined functions. If we substitute this form into (5a), (5b), and (6b) and equate the coefficients of like powers of τ, we find

$$\Xi_1''(\xi) + \Xi_1'(\xi) = 0 \tag{7a}$$

$$\Xi_1'(0) + \Xi_1(0) = 0 \tag{7b}$$

$$\int_0^\infty \Xi_1(\xi)\ d\xi = 1 \tag{7c}$$

$$\Xi_2''(\xi) + \Xi_2'(\xi) = \Xi_1(\xi) \tag{7d}$$

$$\Xi_2'(0) = \Xi_2(0) = -1 \tag{7e}$$

$$\int_0^\infty \Xi_2(\xi)\, d\xi = 0 \tag{7f}$$

From the first three of these equations we see that $\Xi_1(\xi) = e^{-\xi}$ and from the last three that $\Xi_2(\xi) = (1-\xi)e^{-\xi}$. Thus

$$\Gamma_{as}(\xi,\tau) = e^{-\xi}(\tau + 1 - \xi) \tag{8}$$

is the asymptotic solution of Eqs. (5a) and (5b). The concentration polarization at the membrane $\Gamma(o,\tau)$, which is the main quantity of interest here, is therefore asymptotic to $\tau + 1$.

In the problem presently being dealt with, we can also calculate the nonasymptotic (transient) behavior of the concentration polarization at the membrane explicitly. If we define $\Gamma_{tr}(\xi,\tau)$ by

$$\Gamma_{tr}(\xi,\tau) = \Gamma(\xi,\tau) - e^{-\xi}(\tau + 1 - \xi) \tag{9}$$

we find by substituting it into Eqs. (5) that it satisfies the equation

$$\frac{\partial^2\Gamma_{tr}}{\partial\xi^2} + \frac{\partial\Gamma_{tr}}{\partial\xi} = \frac{\partial\Gamma_{tr}}{\partial\tau} \tag{10a}$$

$$\left(\frac{\partial\Gamma_{tr}}{\partial\xi}\right)_{\substack{\xi=0\\ \tau=\tau}} + \Gamma_{tr}(0,\tau) = 0 \tag{10b}$$

$$\Gamma_{tr}(\xi,0) = (\xi-1)e^{-\xi} \tag{10c}$$

We shall solve Eqs. (10) with the help of the Laplace transform.[6] If

$$\bar{\Gamma}_{tr}(\xi,s) = \int_0^\infty e^{-\tau s}\, \Gamma_{tr}(\xi,\tau)\, d\tau \tag{11}$$

(6) Cf. e.g., "Operational Methods in Applied Mathematics," H. S. Carslaw and J. C. Jaeger, Oxford Univ. Press, London, 1948, pp. 1-9.

then $\bar{\Gamma}_{tr}$ satisfies the equation

$$\frac{d^2\bar{\Gamma}_{tr}(\xi,s)}{d\xi^2} + \frac{d\bar{\Gamma}_{tr}(\xi,s)}{d\xi} = s\,\bar{\Gamma}_{tr}(\xi,s) - (\xi-1)e^{-\xi} \tag{12a}$$

$$\left(\frac{d\Gamma_{tr}}{d\xi}\right)_{\substack{\xi=0\\ s=s}} + \bar{\Gamma}_{tr}(0,s) = 0 \tag{12b}$$

the substitution

$$\psi(\xi,s) = \bar{\Gamma}_{tr}(\xi,s)e^{+\xi/2} \tag{13}$$

reduces Eqs. (12) to

$$\frac{d^2\psi}{d\xi^2} - (s + \tfrac{1}{4})\,\psi = -(\xi - 1)e^{-\xi/2} \tag{14a}$$

$$\left(\frac{d\psi}{d\xi}\right)_{\substack{\xi=0\\ s=s}} + \frac{1}{2}\,\psi(0,s) = 0 \tag{14b}$$

Now suppose that $\psi_1(\xi,s)$ and $\psi_2(\xi,s)$ are two linearly independent solutions of the homogeneous equation corresponding to (14a), viz.,

$$\frac{d^2\psi}{d\xi^2} - (s + \tfrac{1}{4})\,\psi = 0 \tag{15}$$

Furthermore, let ψ_1 satisfy the boundary condition (14b) and let ψ_2 be regular at infinity. Since the Wronskian of these two solutions is a constant, the Green's function of (15) is

$$G(\xi,\xi') = \frac{\psi_1(\xi_<)\ \psi_2(\xi_>)}{\psi_2'(o)\ \psi_1(o) - \psi_1'(o)\ \psi_2(o)} \tag{16}$$

where $\xi_<$ is the smaller of ξ and ξ', $\xi_>$ is the larger of ξ and ξ', and the primes on the ψ's denote differentiation with respect to ξ.[7]

(7) "The Mathematics of Physics and Chemistry," H. Margenau and G. M. Murphy, D. Van Nostrand Co., Inc., New York, 1949, p. 516 ff.

Furthermore,

$$G(o,\xi') = \frac{\psi_2(\xi')}{\psi_2'(o) + \frac{1}{2}\ \psi_2(o)} \tag{17}$$

Here we have made use of the fact that ψ_1 satisfies Eq. (14b). From (17) it follows that

$$\bar{\Gamma}_{tr}(0,s) = \psi(0,s) = -\int_o^\infty \frac{\psi_2(\xi)}{\psi_2'(o) + \frac{1}{2}\psi_2(o)}\ (\xi-1)\ e^{-\xi/2}\ d\xi \tag{18}$$

$\bar{\Gamma}_{tr}(0,s)$ is the Laplace transform of $\Gamma_{tr}(o,\tau)$, the concentration polarization at the membrane.

It is clear from Eq. (15) that $\psi_2(\xi) = e^{-\xi\sqrt{s+\frac{1}{4}}}$. Substituting this equation into (18) and carrying out the integral we obtain

$$\bar{\Gamma}_{tr}(o,s) = -\frac{1}{(\sqrt{s+\frac{1}{4}} + \frac{1}{2})^2} \tag{19}$$

Inversion of this Laplace transform[8] now gives

$$\Gamma_{tr}(o,\tau) = -\frac{1}{2\pi i}\int_{-i\infty}^{i\infty} \frac{e^{s\tau}}{(\sqrt{s+\frac{1}{4}} + \frac{1}{2})^2}\quad ds \tag{20}$$

(8) H. S. Carslaw and J. C. Jaeger, op. cit., pp. 71-77.

The only singularity of the integrand is a branch point at $s = -1/4$. If we deform the path of integration to the dotted path shown in Fig. 2, we can express $\Gamma_{tr}(o,\tau)$ as

$$\Gamma_{tr}(o,\tau) = -\frac{1}{\pi}\int_{\frac{1}{4}}^{\infty} \frac{\sqrt{s - \frac{1}{4}}}{s^2} e^{-s\tau}\, ds \tag{21a}$$

$$= -\frac{4}{\pi} e^{-\tau/4} \int_{0}^{\infty} \frac{y^2 e^{-y^2\tau/4}}{(1 + y^2)^2}\, dy \tag{21b}$$

where $y^2 = 4s - 1$. The right-hand side of Eq. (21b) can be evaluated in terms of the complementary error function:

$$\Gamma_{tr}(o,\tau) = -(1 + \tau/2)\ \mathrm{erfc}\ (\sqrt{\tau}/2) + \sqrt{\tau/\pi}\ e^{-\tau/4} \tag{22a}$$

where

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^2}\, du \tag{22b}$$

$\Gamma(o,\tau)$ is shown in Fig. 3.

<u>Continuously Operated Cell; Laminar Flow</u>

The geometry of the continuously operated cell is shown in Fig. 4. The main flow is in the x-direction. The width and length of the channel are presumed to be very much larger than the channel thickness, 2ℓ. A steady state solution of Eq. (1) exists and it is this solution that we now seek.

In laminar channel flow, Eq. (1) becomes

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \mathcal{D} \frac{\partial^2 c}{\partial y^2} \tag{23}$$

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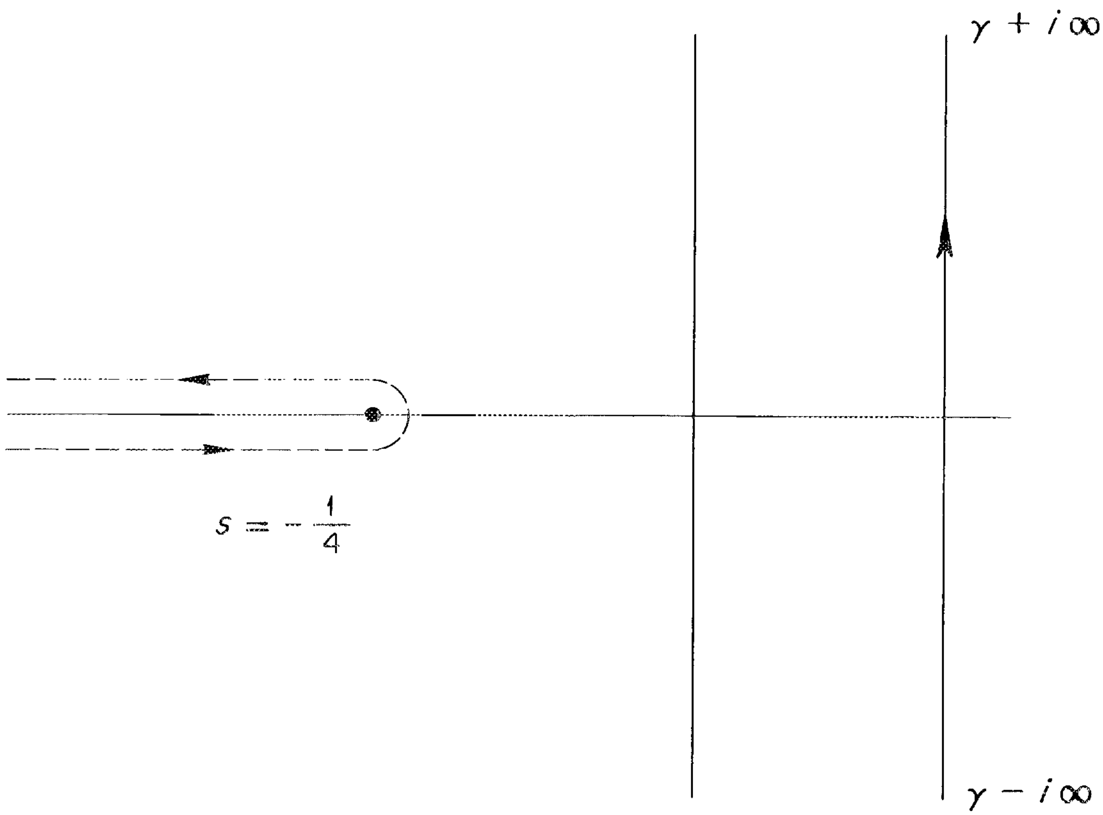

Fig. 2. The Original (Solid) and Deformed (Dotted) Paths of Integration in the Complex s-Plane. The integrand in Eq. (20) has a branch point at $s = -1/4$; the s-plane has consequently been cut along the negative real axis from $s = -1/4$ to $s = -\infty$.

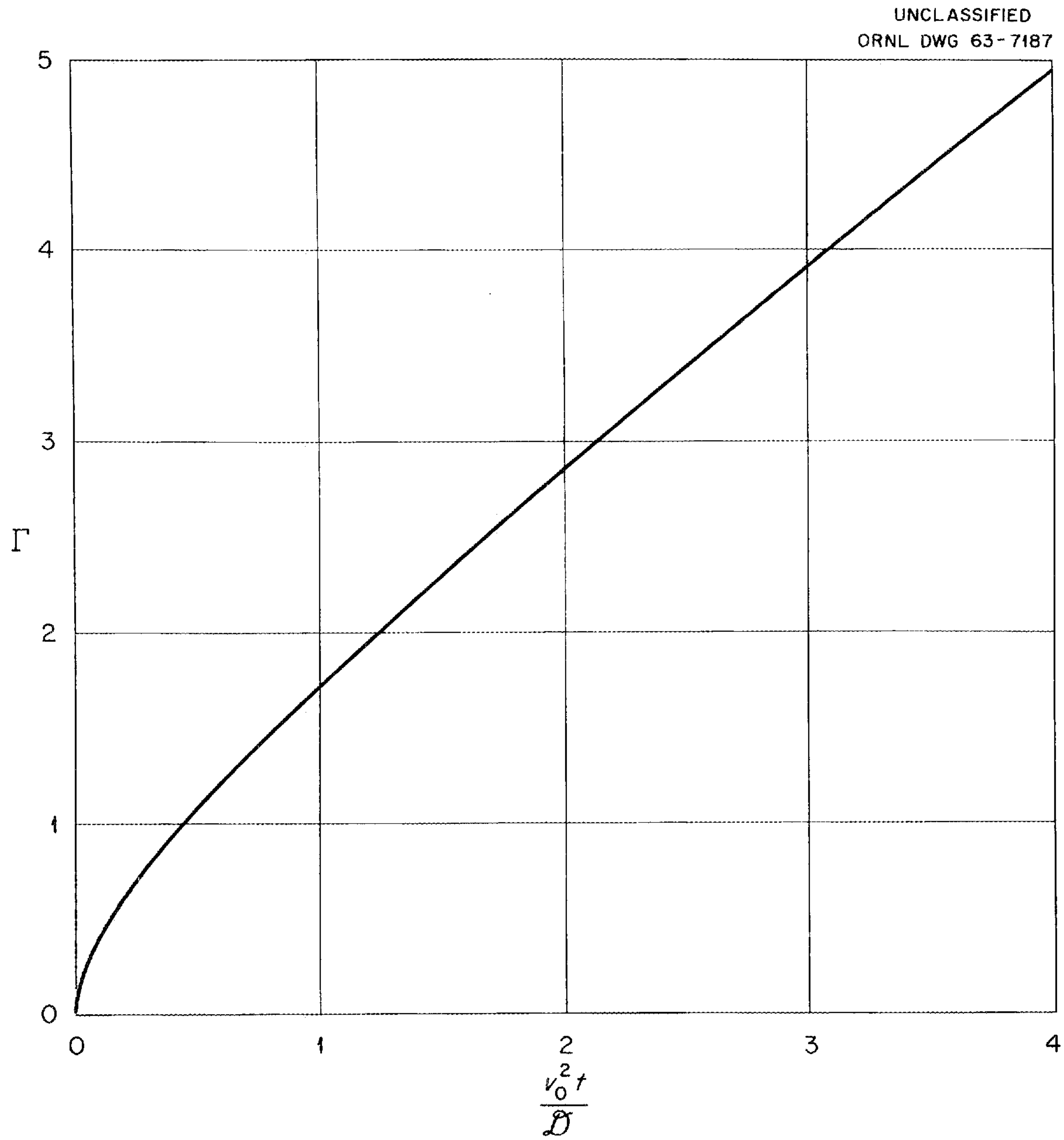

Fig. 3. The Concentration Polarization Γ at the Membrane in the Batch-Operated Cell. Γ is the ratio of the excess salt concentration at the membrane to the initial concentration [cf. Eq. (4a)], v_0 is the constant fluid velocity (cf. Fig. 1), t is the time, and $\mathcal{D}$ is the diffusivity of the salt (cm^2/sec).

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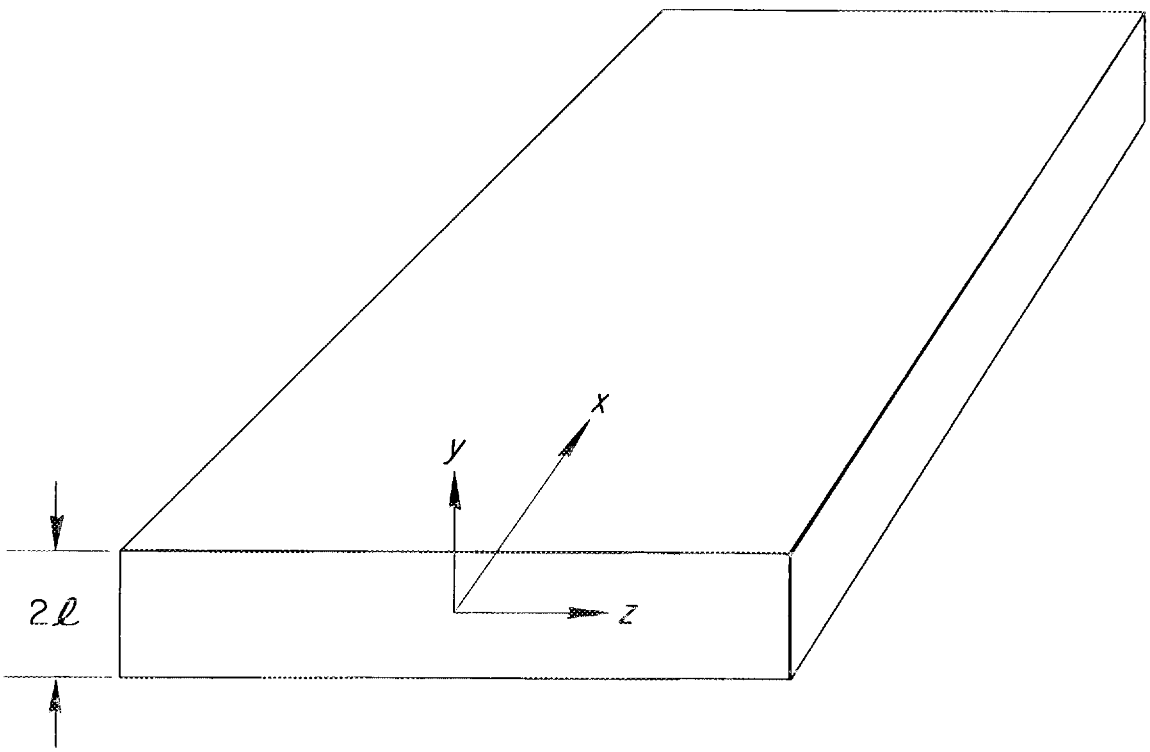

Fig. 4. The Geometry of the Continuously Operated Cell.

The term in $\mathcal{D}\,\partial^2 c/\partial x^2$ has been neglected since axial convection of salt, which is described by the term u $\partial c/\partial x$, far outweighs axial conduction, which is described by the omitted term.[9]

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(9) A similar approximation is made in the classical Graetz-Nusselt problem; cf. "Heat Transfer," Vol. I, M. Jakob, John Wiley and Sons, New York, 1949, p. 451.

According to Berman,[5] the velocity components u and v are given by

$$u = [\bar{u}_o - (v_w x/\ell)]\, f'(\lambda) \tag{24a}$$

$$v = v_w\, f(\lambda) \tag{24b}$$

where $f(\lambda)$ is a function that has been calculated by Berman. The form of these functions suggests that we may be able to solve (23) by the method of separation variables. If we set $c(x,y) = X(x)Y(y)$, we find that (23) can be written

$$\mathcal{D} Y'' - vY' - u_o Y \left(\frac{u}{u_o} \quad \frac{X'}{X}\right) = 0 \tag{25}$$

The factor in parentheses in the last term in (25) depends only on x, while all the other terms in (25) depend only on y. Thus

$$\mathcal{D} Y'' - vY' - \frac{v_w \sigma}{\bar{u}_o \ell} \quad u_o Y = 0 \tag{26a}$$

and

$$\frac{u}{u_o} \; \frac{X'}{X} = \frac{v_w \sigma}{\bar{u}_o \ell} \tag{26b}$$

where, for convenience, the separation constant has been written in the form $\frac{v_w \sigma}{\bar{u}_o \ell}$.

The solution of Eq. (26b) (arbitrarily normalized to the value unity at x = 0) is

$$X = \left(1 - \frac{v_w x}{\bar{u}_o \ell}\right)^{-\sigma} \tag{27}$$

The admissible values of σ are the eigenvalues of Eq. (26a) subject to the conditions

$$Y'(o) = 0 \tag{28a}$$

$$v_w Y(\ell) - \mathcal{D} Y'(\ell) = 0 \tag{28b}$$

Eq. (28a) is a symmetry requirement; Eq. (28b) states the impenetrability of the channel walls to the salt. If for the sake of convenience, we write Eqs. (26a), (28a), and (28b) in terms of the variable $\lambda = y/\ell$, we find

$$Y'' - \alpha f(\lambda) Y' - \alpha\sigma f'(\lambda) Y = 0 \tag{29a}$$

$$Y'(o) = 0 \tag{29b}$$

$$\alpha Y(1) - Y'(1) = 0 \tag{29c}$$

where the primes now denote differentiation with respect to λ. $\alpha = v_w \ell/\mathcal{D}$ is the Péclet number for mass transfer and is equal to the product of the transverse Reynolds number $R_w = v_w \ell/\nu$ and the Schmidt number $S_c = \nu/\mathcal{D}$.

The substitution

$$Y(\lambda) = Y(\lambda) \exp\left(\alpha \int_o^\lambda f(\lambda')d\lambda'\right) \tag{30}$$

leads to a Sturm-Liouville equation for $V(\lambda)$:[10]

(10) H. Margenau and G. M. Murphy, op. cit., pp. 253-267.

$$V'' + \alpha f(\lambda)V' + \alpha(1 - \sigma)\ f'(\lambda)V = 0 \tag{31a}$$

$$V'(o) = V'(1) = 0 \tag{31b}$$

Here we have used the fact that $f(1) = 1$ and $f(o) = 0$. The well-known variational principle[10] for the eigenvalues σ now takes the form

$$1-\sigma = \frac{1}{\alpha}\cdot \frac{\int_o^1 \exp\left(-\alpha\int_\lambda^1 f(\lambda')\ d\lambda'\right) V'^2\ d\lambda}{\int_o^1 f'(\lambda)\ \exp\left(-\alpha\int_\lambda^1 f(\lambda')\ d\lambda'\right)\ V^2\ d\lambda} \tag{32}$$

We can see simply that the eigensolution $V = 1$ satisfies (31a) and (31b) with the eigenvalue $\sigma = 1$. The corresponding value of Y is

$\exp\left(\alpha \int_o^\lambda f(\lambda')\ d\lambda'\right)$. Eq.(32) indicates that $\sigma = 1$ is the <u>largest</u> of the eigenvalues. Eq. (27) shows that it is the $\sigma = 1$ eigensolution which dominates asymptotically for large x. Thus when the <u>concentration profile is fully developed</u>, it is described by

$$\exp\left(\alpha \int_o^\lambda f(\lambda')d\lambda'\right).$$

As an index of the concentration polarization at the membrane we shall take the ratio of the excess wall concentration to the local cup-mixing concentration:

$$\Gamma = \frac{Y(1)\int_0^1 u(\lambda)\,d\lambda}{\int_0^1 u(\lambda)Y(\lambda)d\lambda} - 1 = \frac{Y(1)}{\int_0^1 f'(\lambda)Y(\lambda)d\lambda} - 1 = \frac{1}{\int_0^1 f'(\lambda)\frac{Y(\lambda)}{Y(1)}\,d\lambda} - 1 \tag{33}$$

This is a particularly useful quantity, since if little water is drawn off, the local cup-mixing concentration will differ little from the bulk feed-water concentration.

Cellulose acetate membranes generally permit flow velocities of the order of 5×10^{-4} cm sec^{-1} $\approx$ 10 gals/ft^2/day with pressures of the order of 100 atm. With such small velocities the transverse Reynolds number R_w is $\ll 1$ for reasonable channel thicknesses. When $R_w \ll 1$, Berman[5] has shown that the Poisseuille profile is a very accurate representation of the longitudinal flow and henceforth we shall always use it. Thus $f'(\lambda) = \frac{3}{2}(1-\lambda^2)$ and

$$\Gamma = \frac{1}{\int_0^1 \frac{3}{2}(1-\lambda^2)\exp\left[-\alpha\left(\frac{5}{8} - \frac{3}{4}\lambda^2 + \frac{1}{8}\lambda^4\right)\right] d\lambda} \tag{34}$$

When $\alpha \gg 1$, this integral is easy to evaluate. Γ then becomes approximately $\frac{1}{3}\alpha^2$. Γ is plotted as a function of α in Fig. 5.

x/ℓ can never exceed $\bar{u}_o/v_w$, for in principle when $x = x_\infty = \bar{u}_o\ell/v_w$ all the water has been drawn off through the channel walls. The speed with which the $\sigma = 1$ mode dominates the concentration profile can be characterized by the ratio of the value of x at which the higher modes have fallen to some specified fraction of their initial intensity to the value

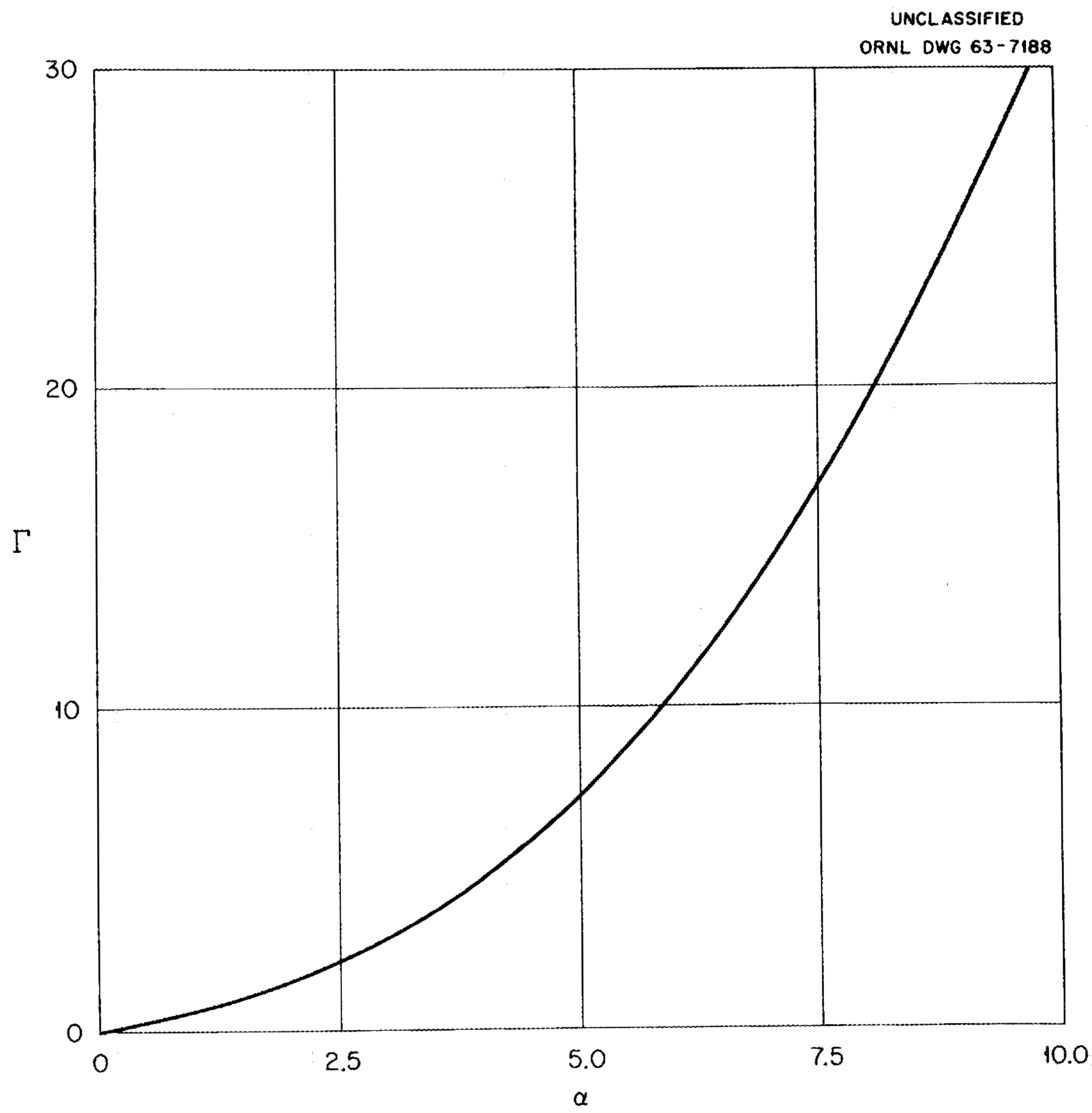

Fig. 5. The Asymptotic Concentration Polarization Γ at the Wall in the Continuously Operated Cell. Γ is the ratio of the excess wall concentration to the local cup-mixing concentration [cf. Eqs. (33) and (34)]; and α is the Pèclet number for mass transfer, defined by $v_w \ell/\mathcal{D}$, where v_w is the fluid suction velocity at the wall, ℓ is the half-thickness of the channel (cf. Fig. 4), and $\mathcal{D}$ is the diffusivity of the salt (cm^2/sec).

x_∞. When σ is large and negative, it is easy to show that any mode will fall to 1% of its initial intensity when $x/x_\infty = 4.6/|\sigma|$. In fact as long as $x/x_\infty \ll 1$, the modes decay exponentially with $1/|\sigma|$ as the decay constants. If any eigenvalue is not large and negative, the corresponding mode will decay slowly, and the $\sigma = 1$ mode will not dominate the solution until x is very close to x_∞.

Table 1 shows the first few eigenvalues of Eqs. (31) for several values of α.

Table 1. Eigenvalues $1-\sigma$ of Eqs. (31) for $\alpha = 1$, 3, and 10

n \ α	1	3	10
1	11.466	3.4529	1.1331
2	44.905	14.472	4.5313
3	99.764	32.647	9.8595

It is clear from these results, that when $\alpha \leq 1$ the ground (σ=1) mode will dominate over most of the range of x, whereas when $\alpha \geq 10$ the asymptotic state is not reached until x nearly equals x_∞. Thus when $\alpha \gg 1$, the asymptotic solution $\exp\left(\alpha \int_0^\lambda f(\lambda')\, d\lambda'\right)$ for the concentration profile is of no practical use. In order to get an expression for the concentration profile valid for small x, let us consider the following situation. A salt solution flows through a channel which sucks liquid through its wall with a velocity v_w. The entrance length of the channel, lying at values of $x < 0$, is long enough to allow the velocity distribution (24) to be established. Throughout its entrance length the channel is equally permeable to water and salt, so that for $x < 0$ the concentration profile is flat. At $x = 0$ the wall of the channel becomes impervious to salt. A thin salt-rich boundary layer begins to build up as the fluid passes the point $x = 0$. When $x/\ell \ll \bar{u}_o/v_w$, the concentration profile in this boundary layer is governed by the equation

$$\bar{u}_o f'(\lambda) \frac{\partial c}{\partial x} + v_w f(\lambda) \frac{\partial c}{\partial y} = \mathcal{D} \frac{\partial^2 c}{\partial y^2} \tag{35}$$

Since the boundary layer is confined to a thin region very close to the wall, $\lambda \approx 1$ and $f'(\lambda)$ and $f(\lambda)$ may be replaced by the leading terms in their respective power series expansions around $\lambda = 1$, viz., $3(1-\lambda)$ and 1 when $R_w \ll 1$.

If we now introduce the dimensionless variables

$$\Gamma = \frac{c - c_o}{c_o} \tag{36a}$$

$$\zeta = \frac{\alpha^2}{3} \frac{v_w}{\bar{u}_o} \frac{x}{\ell} \tag{36b}$$

$$\eta = \alpha(1 - \lambda) \tag{36c}$$

(35) takes the form

$$\frac{\partial^2 \Gamma}{\partial \eta^2} + \frac{\partial \Gamma}{\partial \eta} = \eta \frac{\partial \Gamma}{\partial \zeta} \tag{37a}$$

The boundary conditions are

$$\left(\frac{\partial \Gamma}{\partial \eta} \right)_{\substack{\eta=0 \\ \zeta=\zeta}} + \Gamma(0,\zeta) = -1 \tag{37b}$$

$$\Gamma(\eta,0) = 0 \tag{37c}$$

We can find the asymptotic solution of Eqs. (37) exactly as we found the asymptotic solution of Eqs. (5). The result is

$$\Gamma_{as}(\eta,\zeta) = e^{-\eta}(\zeta + 5 - \eta - \eta^2/2) \tag{38a}$$

so that

$$\Gamma_{as}(0,\zeta) = \zeta + 5. \tag{38b}$$

Again defining $\Gamma_{tr}(\eta,\zeta) = \Gamma(\eta,\zeta) - \Gamma_{as}(\eta,\zeta)$, we find that Γ_{tr} satisfies the equations

$$\frac{\partial^2\Gamma_{tr}}{\partial\eta^2} + \frac{\partial\Gamma_{tr}}{\partial\eta} = \eta\,\frac{\partial\Gamma_{tr}}{\partial\zeta} \tag{39a}$$

$$\left(\frac{\partial\Gamma_{tr}}{\partial\eta}\right)_{\substack{\eta=0\\ \zeta=\zeta}} + \Gamma_{tr}(0,\zeta) = 0 \tag{39b}$$

$$\Gamma_{tr}(\eta,0) = -e^{-\eta}(5 - \eta - \eta^2/2) \tag{39c}$$

We proceed now exactly as we did before. First we Laplace transform Eqs. (39a) and (39b) with respect to ζ; then we make the substitution (13) (with ζ written for ξ). The result of these manipulations is that

$$\bar{\Gamma}_{tr}(o,s) = \int_o^\infty \frac{\psi_2(\eta)}{\psi_2'(o) + \frac{1}{2}\psi_2(o)}\, e^{-\eta/2}\,\eta(5 - \eta - \eta^2/2)\, d\eta \tag{40}$$

where $\psi_2(\eta)$ is the solution of

$$\frac{d^2\psi}{d\eta^2} - (s\eta + \tfrac{1}{4})\,\psi = 0 \tag{41}$$

that is regular at infinity.

Owing to the presence of the factor η multiplying s in (41), ψ_2 cannot now be expressed in terms of simple exponentials: we can verify by substitution that

$$\psi_2(\eta) = \sqrt{s\eta + \tfrac{1}{4}} \; K_{1/3}\left(\frac{2}{3s}\,[s\eta + \tfrac{1}{4}]^{3/2}\right) \tag{42}$$

where $K_{1/3}$ is the modified Bessel function of the second kind of order one-third.[11] A short calculation then shows that

$$\psi_2'(o) + \frac{1}{2}\,\psi_2(o) = \frac{1}{4}\left[\, K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)\right] \tag{43}$$

so that finally

$$\Gamma_{tr}(o,\zeta) = -\int_0^\infty e^{-\eta/2}\,(\eta^3/2 + \eta^2 - 5\eta)\,\mathcal{L}^{-1}\left\{\frac{4\sqrt{\eta s + \frac{1}{4}}\;K_{1/3}\left(\frac{2}{3s}\,[\eta s + \frac{1}{4}]^{3/2}\right)}{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)}\right\} d\eta \tag{44}$$

where $\mathcal{L}^{-1}$ denotes the inverse Laplace transform. According to the inversion theorem[8]

$$\mathcal{L}^{-1}\{\ldots\} = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} \frac{4\sqrt{\eta s + \frac{1}{4}}\;K_{1/3}\left(\frac{2}{3s}\,[\eta s + \frac{1}{4}]^{3/2}\right)}{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)}\, e^{\zeta s}\, ds \tag{45}$$

---

(11) "Bessel Functions," G. N. Watson, Cambridge University Press, The Macmillan Co., New York, 1944.

The explicit inversion of the transform in (45) is well-nigh impossible and to obtain a useful approximation to $\Gamma_{tr}(o,\zeta)$ we must proceed obliquely as follows. The analysis of Appendix 1 shows that when $\zeta \gg 1$ the right-hand side of (45) is asymptotic to $-e^{-\sqrt{2\zeta/3}}$ if $(4\eta)^2 \ll 6\zeta$ and to $e^{-\sqrt{\zeta/3}}$ if $(4\eta)^2 \gg 6\zeta$. These facts suggest that a function of the type $e^{-\sqrt{\zeta/a}}$ might adequately represent the asymptotic behavior of $\Gamma_{tr}(o,\zeta)$. Such a function has the additional virtue of having an infinite derivative at $\zeta = 0$, which the analysis of Appendix 2 indicates $\Gamma_{tr}(o,\zeta)$ must have. Hence we may tentatively set

$$\Gamma_{tr}(o,\zeta) = -5e^{-\sqrt{\zeta/a}} \qquad (45)$$

The value 5 has been chosen for normalization $[\Gamma_{tr}(o,o) = -5]$. The extent to which (46) adequately represents $\Gamma_{tr}(o,\zeta)$ may be determined by seeing how well it reproduces the moments $\int_0^\infty \zeta^k \Gamma_{tr}(o,\zeta)\, d\zeta$ of $\Gamma_{tr}(o,\zeta)$. We can calculate these moments from the Laplace transform (44).[12] The first three

---

(12) The Laplace transform is the generating function of the moments, i.e., $\bar{\Gamma}_{tr}(o,s) = \sum_{k=o}^{\infty} \frac{(-s)^k}{k!} \int_0^\infty \zeta^k\, \Gamma_{tr}(o,\zeta)\, d\zeta$ [cf. Carslaw and Jaeger, op. cit., p. 257, Eq. (1)]. Thus if we expand the Laplace transform (44) in powers of s, we can obtain the various moments of $\Gamma_{tr}(o,\zeta)$ by inspection. Calculating the terms in this series is a tedious job, and a slightly simpler recursive method of calculating the moments can be based on the observation that the quantities $A_k(\eta) = \int_0^\infty \frac{\zeta^k}{k!} \Gamma_{tr}(\eta,\zeta)\, d\zeta$ satisfy the equations

$$\begin{aligned} A_o''(\eta) + A_o'(\eta) &= -\eta\Gamma_{tr}(\eta,o) \\ A_k''(\eta) + A_k'(\eta) &= -\eta A_{k-1}(\eta) \qquad (k \geq 1) \\ A_k'(o) + A_k(o) &= 0 \\ \int_0^\infty \eta A_k(\eta)\, d\eta &= 0 \end{aligned}$$

These equations can be solved successively for A_o, A_1, etc.

moments are -35, -630, and -32690, respectively. Choosing a = 3 makes the first three moments of (46) -30, -540, and -32400, respectively, in comparatively good agreement with the actual moments. Thus

$$\Gamma \ (o,\zeta) \approx \zeta + 5 - 5e^{-\sqrt{\zeta/3}} \tag{46}$$

This function is plotted in Fig. 6.

Continuously Operated Cell; Turbulent Flow

If the axial flow in the channel representing the continuously operated cell is turbulent, the salt concentration at the wall is related to the bulk salt concentration by the following equation:

$$v_w c_o = h(c_w - c_o) \tag{47}$$

so that

$$\Gamma = \frac{c_w - c_o}{c_o} = \frac{v_w}{h} \tag{48}$$

There are a number of semi-empirical expressions relating the mass transfer coefficient to the characteristics of the fluid and the flow pattern; the one we shall use here is that of Chilton and Colburn[13] expressing the

(13) "Mass, Heat, and Momentum Transfer Between Phases," T. K. Sherwood, Chemical Engineering Progress Symposium Series, Vol. 55, No. 25, Reactor Kinetics and Unit Operations, p. 71, 1959. Cf. also reference 14, pp. 401 and 647.

Stanton number in terms of the Schmidt number and the Fanning friction factor:[14]

(14) "Transport Phenomena," R. B. Bird, W. E. Stewart, and E. N. Lightfoot, John Wiley and Sons, New York, 1962, pp. 181-188.

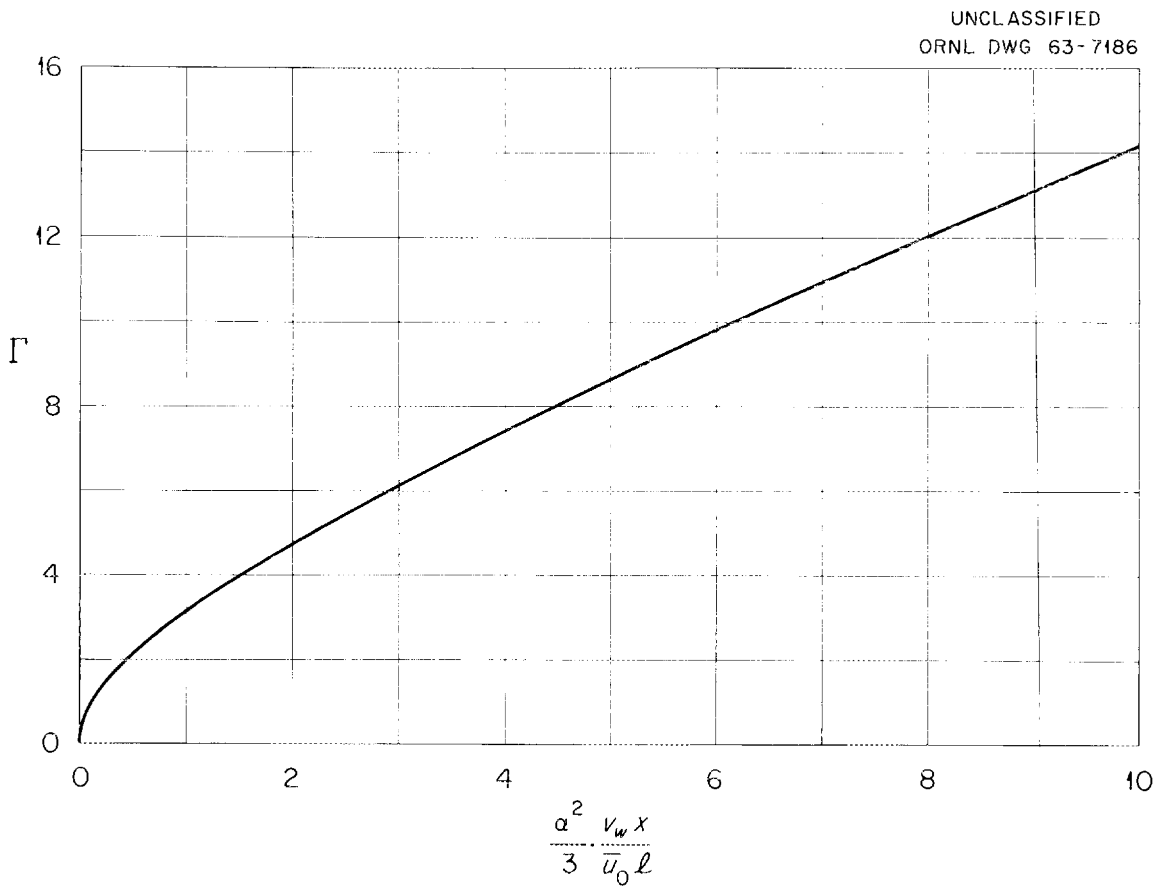

Fig. 6. The Concentration Polarization Γ at the Wall in the Entrance Region of the Continuously Operated Cell. Γ is the ratio of the excess wall concentration to the local cup-mixing concentration [cf. Eq. (36a)]; and α is the Péclet number for mass transfer, defined by $v_W \ell/\mathcal{D}$, where v_W is the fluid suction velocity at the wall, ℓ is the half-thickness of the channel (cf. Fig. 4), and $\mathcal{D}$ is the diffusivity of the salt (cm^2/sec). x is the distance down the channel (cf. Fig. 4), and $\bar{u}_0$ is the bulk fluid velocity in the x-direction.

$$St = \frac{1}{2} f(Sc)^{-2/3} \tag{49}$$

For smooth-walled channels, the friction factor is given by Blasius' equation:[14]

$$f = 0.08 \, (Re)^{-1/4} \tag{50}$$

Combining Eqs. (48), (49), and (50) we have

$$\Gamma = 25 \, (v_w/\bar{u}_o) \, (Re)^{1/4} \, (Sc)^{2/3} \quad . \tag{51}$$

APPENDIX 1

The study of the asymptotic behavior of $\Gamma_{tr}(o,\zeta)$ using the contour integral given in Eq. (45) will require the use of the following properties of the Bessel functions, all of which can either be found in Watson's book[11] or easily deduced from formulas given there.

$$K_{1/3}(re^{i\pi}) = \frac{1}{2} K_{1/3}(r) - i \left[\frac{\sqrt{3}}{2} K_{1/3}(r) + \pi I_{1/3}(r)\right] \qquad (1\text{-}1)$$

$$K_{2/3}(re^{i\pi}) = -\frac{1}{2} K_{2/3}(r) - i \left[\frac{\sqrt{3}}{2} K_{2/3}(r) + \pi I_{2/3}(r)\right] \qquad (1\text{-}2)$$

$$K_{1/3}(re^{-i\pi}) = \overline{K_{1/3}(re^{i\pi})}; \quad K_{2/3}(re^{-i\pi}) = \overline{K_{2/3}(re^{i\pi})} \qquad (1\text{-}3)$$

$$K_{1/3}(re^{-i\pi/2}) = \frac{\pi}{2}\left[J_{-1/3}(r) - J_{1/3}(r)\right] + i\,\frac{\pi}{2\sqrt{3}} \left[J_{-1/3}(r) + J_{1/3}(r)\right] \qquad (1\text{-}4)$$

$$K_{1/3}(re^{i\pi/2}) = \overline{K_{1/3}(re^{-i\pi/2})} \qquad (1\text{-}5)$$

$$K_{1/3}(z) \sim \left(\frac{\pi}{2z}\right)^{1/2} e^{-z}; \quad K_{2/3}(z) \sim \left(\frac{\pi}{2z}\right)^{1/2} e^{-z} \qquad (1\text{-}6)$$

$$I_{1/3}(z) \sim \frac{e^{z}}{(2\pi z)^{1/2}}\ ; \quad I_{2/3}(z) \sim \frac{e^{z}}{(2\pi z)^{1/2}} \qquad (1\text{-}7)$$

$$I_{1/3}(z) - I_{2/3}(z) \sim \frac{e^{z}}{(2\pi z)^{1/2}} \quad \frac{1}{6z} \qquad (1\text{-}8)$$

$$\lim_{z\to 0} \sqrt{z}\; J_{-1/3}(z^{3/2}) = \frac{2^{1/3}}{\Gamma\left(\frac{2}{3}\right)} \qquad (1\text{-}9)$$

$$\lim_{z\to 0} \sqrt{z}\; K_{1/3}(z^{3/2}) = \frac{2^{1/3}}{\sqrt{3}\,\Gamma\left(\frac{2}{3}\right)} \qquad (1\text{-}10)$$

The integrand in (45) has two branch points, one at the origin and the other at the point $s = -1/4\eta$. If we cut the s-plane from o to ∞ along the negative real axis, the path of integration may be deformed to a path similar to that shown in Fig. 2, but enclosing the entire negative real axis.

Then

$$\mathcal{L}^{-1}\{\dots\} = \frac{1}{2\pi i}\int_0^{-\frac{1}{4\eta}} 4\sqrt{\frac{1}{4} - \eta|s|}\left[\frac{K_{1/3}\left(\frac{2e^{-i\pi}}{3|s|}\left[\frac{1}{4}-\eta|s|\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{-i\pi}}{12|s|}\right)-K_{2/3}\left(\frac{e^{-i\pi}}{12|s|}\right)} - \frac{K_{1/3}\left(\frac{2e^{i\pi}}{3|s|}\left[\frac{1}{4}-\eta|s|\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{i\pi}}{12|s|}\right)-K_{2/3}\left(\frac{e^{i\pi}}{12|s|}\right)}\right] e^{\zeta s}\, ds$$

$$+\frac{1}{2\pi i}\int_{-\frac{1}{4\eta}}^{-\infty} 4\sqrt{\eta|s| - \frac{1}{4}}\left[\frac{e^{i\pi/2}K_{1/3}\left(\frac{2e^{i\pi/2}}{3|s|}\left[\eta|s|-\frac{1}{4}\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{-i\pi}}{12|s|}\right)-K_{2/3}\left(\frac{e^{-i\pi}}{12|s|}\right)} - \frac{e^{-i\pi/2}K_{1/3}\left(\frac{2e^{-i\pi/2}}{3|s|}\left[\eta|s|-\frac{1}{4}\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{i\pi}}{12|s|}\right)-K_{2/3}\left(\frac{e^{i\pi}}{12|s|}\right)}\right] e^{\zeta s}\, ds \qquad (1\text{-}11)$$

In both of these integrals the two terms in the brackets are complex conjugates of one another (cf. Eqs. (1-3) and (1-5). Thus replacing s by -s for convenience we can write

$$\mathcal{L}^{-1}\{\dots\} = \frac{4}{\pi}\int_0^{\frac{1}{4\eta}}\sqrt{\frac{1}{4} - \eta s}\ \mathrm{Im}\ \frac{K_{1/3}\left(\frac{2e^{i\pi}}{3s}\left[\frac{1}{4}-\eta s\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{i\pi}}{12s}\right)-K_{2/3}\left(\frac{e^{i\pi}}{12s}\right)}\, e^{-\zeta s}\, ds - \frac{4}{\pi}\int_0^{\infty}\sqrt{\eta s - \frac{1}{4}}\ \mathrm{Re}\ \frac{K_{1/3}\left(\frac{2e^{-i\pi/2}}{3s}\left[\eta s-\frac{1}{4}\right]^{3/2}\right)}{K_{1/3}\left(\frac{e^{i\pi}}{12s}\right)-K_{2/3}\left(\frac{e^{i\pi}}{12s}\right)}\, e^{-\zeta s}\, ds \qquad (1\text{-}12)$$

Using Eqs. (1-1), (1-2), and (1-4) we can rewrite Eq. (1-12) as

$$\mathcal{L}^{-1}\{\ldots\} = \frac{4}{\pi}\int_{0}^{\frac{1}{4\eta}} \sqrt{\frac{1}{4} - \eta s}\; e^{-\zeta s} \Bigg[\Bigg\{ \frac{1}{2} K_{1/3}\left(\frac{2}{3s}\left[\frac{1}{4} - \eta s\right]^{3/2}\right)\left[\frac{\sqrt{3}}{2}\left\{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)\right\} + \pi\left\{I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right)\right\}\right]$$

$$- \frac{1}{2}\left[K_{1/3}\left(\frac{1}{12s}\right) + K_{2/3}\left(\frac{1}{12s}\right)\right]\left[\frac{\sqrt{3}}{2} K_{1/3}\left(\frac{2}{3s}\left[\frac{1}{4} - \eta s\right]^{3/2}\right) + \pi\, I_{1/3}\left(\frac{2}{3s}\left[\frac{1}{4} - \eta s\right]^{3/2}\right)\right]\Bigg\} \Bigg/ \Bigg\{\frac{1}{4}\left[K_{1/3}\left(\frac{1}{12s}\right) + K_{2/3}\left(\frac{1}{12s}\right)\right]^{2}$$

$$+ \left[\frac{\sqrt{3}}{2}\left\{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)\right\} + \pi\left\{I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right)\right\}\right]^{2}\Bigg\}\Bigg]\, ds$$

$$- \frac{4}{\pi}\int_{\frac{1}{4\eta}}^{\infty} \sqrt{\eta s - \frac{1}{4}}\; e^{-\zeta s} \Bigg[\Bigg\{ \frac{\pi}{4}\left[K_{1/3}\left(\frac{1}{12s}\right) + K_{2/3}\left(\frac{1}{12s}\right)\right]\left[J_{-1/3}\left(\frac{2}{3s}\left[\eta s - \frac{1}{4}\right]^{3/2}\right) - J_{1/3}\left(\frac{2}{3s}\left[\eta s - \frac{1}{4}\right]^{3/2}\right)\right] \frac{\pi}{2\sqrt{3}}\left[\frac{\sqrt{3}}{2}\left\{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)\right\}\right.$$

$$\left. + \pi\left\{I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right)\right\}\right]\left[J_{-1/3}\left(\frac{2}{3s}\left[\eta s - \frac{1}{4}\right]^{3/2}\right) + J_{1/3}\left(\frac{2}{3s}\left[\eta s - \frac{1}{4}\right]^{3/2}\right)\right]\Bigg\} \Bigg/ \Bigg\{\frac{1}{4}\left[K_{1/3}\left(\frac{1}{12s}\right) + K_{2/3}\left(\frac{1}{12s}\right)\right]^{2} \tag{1-13}$$

$$+ \left[\frac{\sqrt{3}}{2}\left\{K_{1/3}\left(\frac{1}{12s}\right) - K_{2/3}\left(\frac{1}{12s}\right)\right\} + \pi\left\{I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right)\right\}\right]^{2}\Bigg\}\Bigg]\, ds$$

When $\zeta \gg 1$, the main contribution to the first integral comes from very small values of s. If s is very small, $\frac{1}{12s} \gg 1$, and we can replace the various Bessel functions by their asymptotic values. If we keep only the leading terms in both numerator and denominator, we find that the first integrand is simply

$$- \frac{e^{-\zeta s}}{4\pi} \frac{K_{1/3}\left(\frac{1}{12s}\right) I_{2/3}\left(\frac{1}{12s}\right) + K_{2/3}\left(\frac{1}{12s}\right) I_{1/3}\left(\frac{1}{12s}\right)}{\left[I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right)\right]^{-2}} \sim - \frac{e^{-(\zeta s + 1/6s)}}{8s^2} \tag{1-14}$$

so that the first integral can be written

$$- \frac{1}{2\pi} \int_0^{\frac{1}{4\eta}} e^{-(\zeta s + 1/6s)} \frac{ds}{s^2} \tag{1-15}$$

If $6\zeta \gg (4\eta)^2$, we can evaluate this integral by the method of steepest descents. If we set $s = (6\zeta)^{-1/2} + \epsilon$ then

$$\zeta s + \frac{1}{6s} = \sqrt{2\zeta/3} + \zeta \sqrt{6\zeta}\, \epsilon^2 + \ldots \tag{1-16}$$

so that the first integral finally becomes

$$- \frac{3\zeta}{\pi} e^{-\sqrt{2\zeta/3}} \int_{-\infty}^{+\infty} e^{-\zeta\sqrt{6\zeta}\, \epsilon^2} d\epsilon = - \frac{3}{6^{1/4} \sqrt{\pi}} \zeta^{1/4} e^{-\sqrt{2\zeta/3}} = -1.082\zeta^{1/4} e^{-\sqrt{2\zeta/3}} \tag{1-17}$$

The second integral is of the order of $e^{-\zeta/4\eta}$, which because of the condition $(6\zeta) \gg (4\eta)^2$ is $\ll e^{-\sqrt{2\zeta/3}}$. Hence for not-too-large η, Eq. (1-17) represents the asymptotic behavior of $\mathcal{L}^{-1}\left\{\ldots\right\}$.

If $(4\eta)^2 \gg 6\zeta$, on the other hand, the first integral can no longer be evaluated by steepest descents. However, under the given condition,

ζs is $\ll 1/6s$, so that the first integral just becomes

$$- \frac{1}{2\pi} \int_{0}^{\frac{1}{4\eta}} e^{-\frac{1}{6s}} \frac{ds}{s^2} = - \frac{3}{\pi} e^{-2\eta/3} \tag{1-18}$$

Since $1/4\eta \ll 1$, the main contribution to the second integral comes from small values of s and it can be written approximately as

$$- \frac{4}{\pi} \int_{\frac{1}{4\eta}}^{\infty} e^{-\zeta s} \frac{\left(- \frac{\pi}{2\sqrt{3}}\right) \lim\limits_{s\to 1/4} \sqrt{\eta s - \frac{1}{4}}\; J_{-1/3}\left(\frac{2}{3s}[\eta s - \frac{1}{4}]^{3/2}\right)}{\pi \left[I_{1/3}\left(\frac{1}{12s}\right) - I_{2/3}\left(\frac{1}{12s}\right) \right]} ds$$

$$\sim \frac{1}{3^{2/3}\sqrt{2\pi}\,\Gamma\left(\frac{2}{3}\right)} \int_{0}^{\infty} e^{-\zeta s - 1/12s} s^{-7/6} ds = \frac{\left(\frac{4}{3}\right)^{1/3}}{\sqrt{2}\;\Gamma\left(\frac{2}{3}\right)} \zeta^{-1/6} e^{-\sqrt{\zeta/3}}$$

$$= 0.5748\, \zeta^{-1/6} e^{-\sqrt{\zeta/3}} \tag{1-19}$$

where the integral has again been evaluated by the method of steepest descents. This last expression is $\gg$ the right-hand side of (1-18) since $(4\eta)^2 \gg 6\zeta$.

APPENDIX 2

In this appendix we shall investigate the behavior of $\Gamma(\eta,\zeta)$ near $\zeta = 0$. Let us look for a solution of Eqs. (37) of the form

$$\Gamma(\eta,\zeta) = F(\zeta)\; G\left(-\frac{\eta^3}{9\zeta}\right) \tag{2-1}$$

Substituting (2-1) into (37a) we find after some simple algebra

$$w\,\frac{G''(w)}{G(w)} + \left(\frac{2}{3} + \frac{\eta}{3} - w\right)\frac{G'(w)}{G(w)} = -\frac{\zeta\, F'(\zeta)}{F(\zeta)} \tag{2-2}$$

where $w = -\eta^3/9\zeta$. Since η and ζ are independent variables, we must clearly have $F(\zeta) = \zeta^{-\kappa}$ and

$$wG''(w) + \left(\frac{2}{3} - w + \frac{\eta}{3}\right) G'(w) - \kappa\, G(w) = 0 \tag{2-3}$$

When $\zeta \ll 1$, the term $\eta/3$ in the parenthesis in the second term of (2-3) can be neglected, for when $\eta \ll 1$, $\eta/3 \ll 2/3$, and when $\eta \gg 1$, $\eta/3 \ll |w| = \eta^3/9\zeta$. Thus G is given by the <u>ordinary</u> differential equation

$$wG''(w) + \left(\frac{2}{3} - w\right) G'(w) - \kappa\, G(w) = 0 \tag{2-4}$$

Eq. (2-4) is the confluent hypergeometric equation and has as its solution

$$G(w) = a_1\; {}_1F_1\left(\kappa,\frac{2}{3},w\right) + a_2\, w^{1/3}\; {}_1F_1\left(\kappa + \frac{1}{3}, \frac{4}{3}, w\right) \tag{2-5}$$

where ${}_1F_1$ is Pochhammer's confluent hypergeometric function,[15] and a_1 and a_2 are constants. Thus

$$\Gamma(\eta,\zeta) = \zeta^{-\kappa}\left[a_1\; {}_1F_1\left(\kappa,\frac{2}{3}, -\frac{\eta^3}{9\zeta}\right) - \frac{a_2\eta}{(9\zeta)^{1/3}}\; {}_1F_1\left(\kappa + \frac{1}{3}, \frac{4}{3}, -\frac{\eta^3}{9\zeta}\right)\right] \tag{2-6}$$

(15) "Methods of Theoretical Physics," P. M. Morse and H. Feshbach, McGraw-Hill Book Co., New York, 1953, pp. 604-606.

It follows from Eq. (2-6) that

$$\Gamma(o,\zeta) = a_1\ \zeta^{-\kappa} \tag{2-7a}$$

$$\left(\frac{\partial\Gamma}{\partial\eta}\right)_{\substack{\eta=0\\ \zeta=\zeta}} = -a_2\ \zeta^{-\kappa}\ (9\zeta)^{-1/3} \tag{2-7b}$$

When $\zeta \ll 1$, the boundary condition (37b) will be nearly satisfied if $\kappa = -\frac{1}{3}$ and $a_2 = \sqrt[3]{9}$. Thus when $\zeta \ll 1$,

$$\Gamma(\eta,\zeta) = a_1\ \zeta^{1/3}\ {}_1F_1\left(-\frac{1}{3},\ \frac{2}{3},\ -\frac{\eta^3}{9\zeta}\right) - \eta \tag{2-8}$$

The constant a_1 can be determined from the requirement that $\Gamma(\eta,\zeta)$ vanish for large η. The confluent hypergeometric function ${}_1F_1(-\frac{1}{3},\ \frac{2}{3},w)$ has the integral representation[16]

---

(16) P. M. Morse and H. Feshbach, ibid, p. 608.

$${}_1F_1(-\frac{1}{3},\ \frac{2}{3},w) = \Gamma(\tfrac{2}{3})(-w)^{1/3} + \frac{\Gamma(\frac{2}{3})}{\Gamma(-\frac{1}{3})}\, w^{-1}\, e^{w}\int_0^\infty e^{-x}\left(1 - \frac{x}{w}\right)^{-\frac{4}{3}} dx \tag{2-9a}$$

so that if $\eta \gg 1$,

$${}_1F_1\left(-\frac{1}{3},\ \frac{2}{3},\ -\frac{\eta^3}{9\zeta}\right) \sim \frac{\eta\Gamma(\frac{2}{3})}{(9\zeta)^{1/3}} + O(e^{-\eta^3/9\zeta}) \tag{2-9b}$$

Using (2-9b) in (2-8) we find that a_1 must equal $\sqrt[3]{9}\big/\Gamma(\frac{2}{3}) = 1.536$.

Notation

a = a constant defined in the text following Eq. (45).

a_1, a_2 = arbitrary constants defined in Eq. (2-5) of Appendix 2.

c = salt concentration at the membrane (moles/liter).

c_o = initial concentration in the batch-operated cell or feed concentration in the continuously operated cell (moles/liter).

c_w = salt concentration at the membrane (moles/liter).

$\mathcal{D}$ = salt diffusivity (cm^2/sec).

$f(\lambda)$ = Berman's function (cf. Ref. 5).

F, G = functions introduced in Eq. (2-1).

${}_1F_1$ = Pochhammer's confluent hypergeometric function (cf. Ref. 14).

h = mass transfer coefficient (cm/sec).

$K_{1/3}$ = modified Bessel function of the second kind of order one-third (cf. Ref. 11).

ℓ = channel half-thickness (cm).

R_w = transverse Reynolds number = $v_w \ell / \nu$.

s = Laplace transform variable.

Sc = Schmidt number = $\nu/\mathcal{D}$.

St = Stanton number = $h/\bar{u}_o$.

t = time (sec).

u = x-component of fluid velocity (cm/sec).

u_o = $u(x=o)$ (cm/sec).

$\bar{u}_o$ = average of u_o over the channel cross section (cm/sec).

$\underset{\sim}{v}$ = fluid velocity vector (cm/sec).

v = y-component of the fluid velocity (cm/sec).

v_o = constant fluid velocity in the batch-operated cell (cm/sec).

v_w = $v(y = \pm \ell)$ (cm/sec).

V = a function defined in Eq. (30).

x, y, z = cartesian coordinates (cm).

x_∞ = $\bar{u}_o \ell / v_w$.

X, Y = functions defined in the text following Eq. (24).

w = $-\eta^3/9\zeta$.

α = Péclet number for mass transfer = $v_w \ell/\mathcal{D}$.

γ = a positive constant.

$\Gamma(\ )$ = the gamma function.

Γ = concentration polarization [cf Eqs. (4a), (33), (36a), and (48).]

Γ_{as} = asymptotic part of Γ [cf. Eqs. (8) and (38).]

Γ_{tr} = transient part of Γ [cf. Eqs. (9) and the text following Eq. (38).]

$\bar{\Gamma}_{tr}$ = Laplace transform Γ_{tr}.

ϵ = an auxiliary quantity introduced in the text preceding Eq. (1-16).

ζ = $\alpha^2 v_w x/3\bar{u}_o \ell$.

η = $1 - \lambda = 1 - y/\ell$.

κ = a number defined in the text following Eq. (2-2).

λ = y/ℓ.

ν = kinematic viscosity (cm^2/sec).

ξ = $v_o x/\mathcal{D}$.

Ξ_1, Ξ_2 = functions defined in the text following Eq. (6b).

σ = eigenvalue of Eqs. (31).

τ = $v_o^2 t/\mathcal{D}$.

ψ = a function defined in Eq. (13).

ψ_1, ψ_2 = functions defined in the text following Eqs. (14); cf. also Eqs. (40) and (41).

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